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(54) High strength composite.

(57) An article made from at least one network of high strength fibers and a thermoplastic polyurethane matrix material derived from an aliphatic diisocyanate and a polyol. Preferably, the article is made from at least one prepreg element which includes at least two adjacent layers of the high strength fiber network in the thermoplastic polyurethane matrix material.

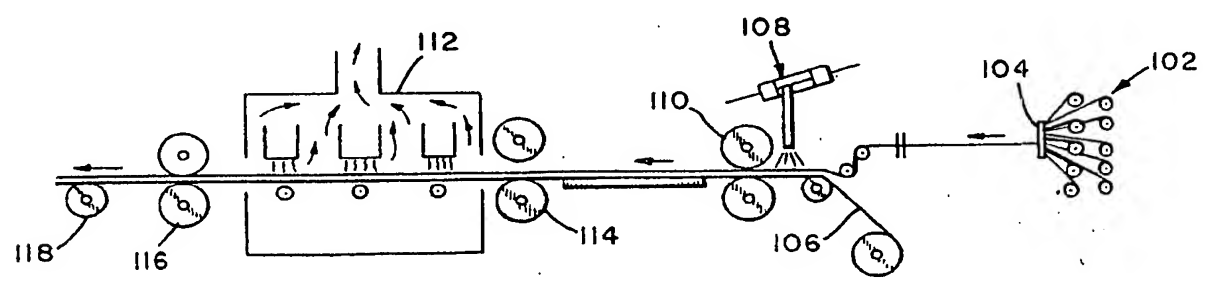


FIG. 1

EP 0 645 415 A1

BACKGROUND OF THE INVENTION

The present invention relates to a composite, particularly one that can be used in sails and ballistic resistant articles, which includes a network of high strength fibers in a polyurethane matrix material.

Various constructions are known for ballistic resistant composites used in ballistic resistant articles such as helmets, panels, and vests. These composites display varying degrees of resistance to penetration by high speed impact from projectiles such as BB's, bullets, shells, shrapnel, glass fragments and the like. U.S. Patents No. 5,196,252; 5,187,023; 5,185,195; 5,175,040; 5,167,876; 5,124,195; 5,112,667; 5,061,545; 5,006,390; 4,953,234; 4,916,000; 4,883,700; 4,820,568; 4,748,064; 4,737,402; 4,737,401; 4,681,792; 4,650,710; 4,623,574; 4,613,535; 4,584,347; 4,563,392; 4,543,286; 4,501,856; 4,457,985; and 4,403,012 and PCT Publication No. WO 91/12136 describe ballistic resistant composites which include high strength fibers made from materials such as extended chain ultra-high molecular weight polyethylene. Typically these fibers are coated, embedded or impregnated in a polymeric matrix material. Of particular interest among the above disclosures is the description of the materials that can be used for the matrix material that is found in PCT Publication No. WO 91/12136 and at column 14, lines 48-58, of U.S. Patent No. 5,167,876; column 4, line 65 to column 5, line 6, of U.S. Patent No. 5,187,023; and column 5, lines 1-11 of U.S. Patent No. 5,196,252.

During production of such composites the matrix materials must be dissolved in a solvent so that they are in a liquid form for application to the high strength fibers. The solvent then must be removed, usually by drying, in order to fabricate the composite. A problem with prior matrix materials is that they require organic solvents which have a high boiling point, thus necessitating more energy and time for removal of the solvent. A further problem with many of the organic solvents is that they require strict handling and disposal procedures because of potential environmental or health hazards.

A need exists, therefore, for new matrix materials which do not require such troublesome solvents, but which provide at least the same level of ballistic performance, mechanical performance and chemical resistance as those presently used.

A need also exists for a sailcloth component that is flexible, exhibits chemical resistance to the ambient elements such as saltwater, and has good adhesion to other sailcloth components.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a composite which includes a matrix material that utilizes a more convenient solvent, but offers a high level of ballistic performance, mechanical performance and chemical resistance. In accomplishing the foregoing object there is provided according to the present invention an article comprising a network of high strength fibers in a matrix material, the high strength fibers having a tenacity of at least about 7 g/d, a tensile modulus of at least about 150 g/d and an energy-to-break of at least about 8 J/g, wherein the matrix material comprises a thermoplastic polyurethane derived from an aliphatic diisocyanate and a polyol. In a preferred embodiment the article is a ballistic resistant article such as a helmet which includes more than one layer of the high strength fiber network in the thermoplastic polyurethane matrix material. In another preferred embodiment the article is a sail which includes at least one layer of the high strength fiber network in the thermoplastic polyurethane matrix material.

There also is provided according to the invention a prepreg element which includes at least two layers of the high strength fiber network in the thermoplastic polyurethane matrix material. A plurality of such prepreg elements can be molded into a composite.

Further objects, features and advantages of the present invention will become apparent from the detailed description of preferred embodiments that follows.

BRIEF DESCRIPTION OF THE DRAWING

The invention will be described below in more detail with reference to the drawing, wherein:

Figure 1 is a schematic representation of a process for making a fiber network layer of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides an improved composite which is particularly useful in ballistic resistant "hard" armor articles. By "hard" armor is meant an article, such as a helmet or panels for military vehicles, which has sufficient mechanical strength so that it maintains structural rigidity when subjected to a

significant amount of stress and is capable of being free-standing without collapsing.

As used herein, "fiber" denotes an elongate body, the length dimension of which is much greater than the transverse dimensions of width and thickness. Accordingly, "fiber" includes monofilament, multifilament, ribbon, strip, staple and other forms of chopped, cut or discontinuous fiber and the like having regular or irregular cross-sections. "Fiber" includes a plurality of any one of the above or a combination of the above.

The cross-sections of filaments for use in this invention may vary widely. They may be circular, flat or oblong in cross-section. They also may be of irregular or regular multi-lobal cross-section having one or more regular or irregular lobes projecting from the linear or longitudinal axis of the filament. It is particularly preferred that the filaments be of substantially circular, flat or oblong cross-section, most preferably the former.

As used herein, "fiber network" denotes a plurality of fibers arranged into a predetermined configuration or a plurality of fibers grouped together to form a twisted or untwisted yarn, which yarns are arranged into a predetermined configuration. The fiber network can have various configurations. For example, the fibers or yarn may be formed as a felt or other nonwoven, knitted or woven into a network, or formed into a network by any conventional techniques. According to a particularly preferred network configuration, the fibers are unidirectionally aligned so that they are substantially parallel to each other along a common fiber direction.

High strength fibers for use in this invention are those having a tenacity equal to or greater than about 7 g/d, a tensile modulus equal to or greater than about 150 g/d and an energy-to-break equal to or greater than about 8 Joules/gram (J/g). Preferred fibers are those having a tenacity equal to or greater than about 10 g/d, a tensile modulus equal to or greater than about 200 g/d and an energy-to-break equal to or greater than about 20 J/g. Particularly preferred fibers are those having a tenacity equal to or greater than about 16 g/d, a tensile modulus equal to or greater than about 400 g/d, and an energy-to-break equal to or greater than about 27 J/g. Amongst these particularly preferred embodiments, most preferred are those embodiments in which the tenacity of the fibers is equal to or greater than about 22 g/d, the tensile modulus is equal to or greater than about 900 g/d, and the energy-to-break is equal to or greater than about 27 J/g. In the practice of this invention, fibers of choice have a tenacity equal to or greater than about 28 g/d, the tensile modulus is equal to or greater than about 1200 g/d and the energy-to-break is equal to or greater than about 40 J/g.

Useful high strength fibers include extended chain polyolefin fibers, particularly extended chain polyethylene (ECPE) fibers, aramid fibers, polyvinyl alcohol fibers, polyacrylonitrile, liquid crystal copolyester, glass and carbon fibers.

U.S. Patent No. 4,457,985 generally discusses such extended chain polyethylene and polypropylene fibers, and the disclosure of this patent is hereby incorporated by reference to the extent that it is not inconsistent herewith. In the case of polyethylene, suitable fibers are those of weight average molecular weight of at least 150,000, preferably at least one million and more preferably between two million and five million. Such extended chain polyethylene fibers may be grown in solution as described in U.S. Pat. No. 4,137,394 to Meihuizen et al., or U.S. Pat. No. 4,356,138 of Kavesh et al., issued Oct. 26, 1982, or a filament spun from a solution to form a gel structure, as described in German Off. No. 3,004, 699 and GB No. 2051667, and especially as described in U.S. Pat. No. 4,413,110. As used herein, the term of polyethylene shall mean a predominantly linear polyethylene material that may contain minor amounts of chain branching or comonomers not exceeding 5 modifying units per 100 main chain carbon atoms, and that may also contain admixed therewith not more than about 50 wt % of one or more polymeric additives such as alkene-1-polymers, in particular low density polyethylene, polypropylene or polybutylene, copolymers containing mono-olefins as primary monomers, oxidized polyolefins, graft polyolefin copolymers and polyoxymethylenes, or low molecular weight additives such as anti-oxidants, lubricants, ultra-violet screening agents, colorants and the like which are commonly incorporated by reference. Depending upon the formation technique, the draw ratio and temperatures, and other conditions, a variety of properties can be imparted to these filaments. The tenacity of the filaments should be at least 15 grams/denier, preferably at least 20 grams/denier, more preferably at least 25 grams/denier and most preferably at least 30 grams/denier. Similarly, the tensile modulus of the filaments, as measured by an Instron tensile testing machine, is at least 300 grams/denier, preferably at least 500 grams/denier and more preferably at least 1,000 grams/denier and most preferably at least 1,200 grams/denier. These highest values for tensile modulus and tenacity are generally obtainable only by employing solution grown or gel filament processes. Many of the filaments have melting points higher than the melting point of the polymer from which they were formed. Thus, for example, high molecular weight polyethylene of 150,000, one million and two million generally have melting points in the bulk of 138°C. The highly oriented polyethylene filaments made of these materials have melting points of from about 7°C to about 13°C higher. Thus, a slight increase in

melting point reflects the crystalline perfection and higher crystalline orientation of the filaments as compared to the bulk polymer.

Similarly, highly oriented extended chain polypropylene fibers of weight average molecular weight at least 200,000, preferably at least one million and more preferably at least two million may be used. Such extended chain polypropylene may be formed into reasonably well oriented filaments by the techniques prescribed in the various references referred to above, and especially by the technique of U.S. Pat. No. 4,413,110. Since polypropylene is a much less crystalline material than polyethylene and contains pendant methyl groups, tenacity values achievable with polypropylene are generally substantially lower than the corresponding values for polyethylene. Accordingly, a suitable tenacity is at least 8 grams/denier, with a preferred tenacity being at least 11 grams/denier. The tensile modulus for polypropylene is at least 160 grams/denier, preferably at least 200 grams/denier. The melting point of the polypropylene is generally raised several degrees by the orientation process, such that the polypropylene filament preferably has a main melting point of at least 168°C., more preferably at least 170°C. The particularly preferred ranges for the above-described parameters can advantageously provide improved performance in the final article. Employing fibers having a weight average molecular weight of at least about 200,000 coupled with the preferred ranges for the above-described parameters (modulus and tenacity) can provide advantageously improved performance in the final article.

High molecular weight polyvinyl alcohol (PV-OH) fibers having high tensile modulus are described in U.S. Pat. No. 4,440,711 to Y. Kwon, et al., which is hereby incorporated by reference to the extent it is not inconsistent herewith. High molecular weight PV-OH fibers should have a weight average molecular weight of at least about 200,000. Particularly useful PV-OH fibers should have a modulus of at least about 300 g/denier, a tenacity of at least about 7 g/denier (preferably at least about 10 g/denier, more preferably at about 14 g/denier and most preferably at least about 17 g/denier), and an energy to break of at least about 8 joules/g. PV-OH fibers having a weight average molecular weight of at least about 200,000, a tenacity of at least about 10 g/denier, a modulus of at least about 300 g/denier, and an energy to break of about 8 joules/g are more useful in producing a ballistic resistant article. PV-OH fiber having such properties can be produced, for example, by the process disclosed in U.S. Pat. No. 4,599,267.

In the case of polyacrylonitrile (PAN), the PAN fiber should have a weight average molecular weight of at least about 400,000. Particularly useful PAN fiber should have a tenacity of at least about 10 g/denier and an energy to break of at least about 8 joule/g. PAN fiber having a molecular weight of at least about 400,000, a tenacity of at least about 15 to 20 g/denier and an energy to break of at least about 8 joule/g is most useful; and such fibers are disclosed, for example, in U.S. Pat. No. 4,535,027.

In the case of aramid fibers, suitable aramid fibers formed principally from aromatic polyamide are described in U.S. Pat. No. 3,671,542, which is hereby incorporated by reference. Preferred aramid fibers will have a tenacity of at least about 20 g/d, a tensile modulus of at least about 400 g/d and an energy-to-break at least about 8 joules/gram, and particularly preferred aramid fibers will have a tenacity of at least about 20 g/d, and an energy-to-break of at least about 20 joules/gram. Most preferred aramid fibers will have a tenacity of at least about 20 g/denier, a modulus of at least about 900 g/denier and an energy-to-break of at least about 30 joules/gram. For example, poly(phenylenediamine terephthalamide) filaments produced commercially by Dupont Corporation under the trade name of Kevlar® 29 and 49 and having moderately high moduli and tenacity values are particularly useful in forming ballistic resistant composites. (Kevlar® 29 has 500 g/denier and 22 g/denier and Kevlar® 49 has 1000 g/denier and 22 g/denier as values of modulus and tenacity, respectively). Also useful in the practice of this invention is poly(metaphenylene isophthalamide) filaments produced commercially by Dupont under the trade name Nomex®.

In the case of liquid crystal copolyesters, suitable fibers are disclosed, for example, in U.S. Patents No. 3,975,487; 4,118,372 and 4,161,470.

According to the invention the high strength fiber network is impregnated or embedded in a thermoplastic polyurethane matrix material derived from a reaction of an aliphatic diisocyanate and a polyol. Such polyurethanes are described in general in Kirk-Othmer, Encyclopedia of Chemical Technology, pp. 576-608 (3rd Ed. 1983). Illustrative aliphatic diisocyanates include hexamethylene diisocyanate, trimethyl hexamethylene diisocyanate, hydrogenated 4,4'-methylene diisocyanate, m-trimethyl xylylene diisocyanate and isophorone diisocyanate. Particularly preferred is a combination of hexamethylene diisocyanate and isophorone diisocyanate. Particularly preferred polyols are polyester polyols which are well known in the art and are described, for example, in U.S. Patent No. 4,954,199. The polyurethane matrix material should have a tenacity of about 1300 to 1900 psi (8970 to 13110 kPa), a tensile modulus (at 100% elongation) of about 190 to 250 psi (1311 to 1725 kPa), a tensile modulus (at 300% elongation) of about 375 to 450 psi (2587 to 3105 kPa), a T_g (as evidenced by a sudden drop in the ductility and elasticity of the material) of less than about 80°C, and an elongation-to-break of at least about 650 to 1000%. Preferably, the polyurethane

material has a tenacity of about 1500 to 1700 psi (10350 to 11730 kPa), a tensile modulus (at 100% elongation) of about 210 to 230 psi (1449 to 1587 kPa), a tensile modulus (at 300% elongation) of about 400 to 425 psi (2760 to 2932 kPa), a T_g (as evidenced by a sudden drop in the ductility and elasticity of the material) of less than about 80 °C, and an elongation-to-break of at least about 750 to 900%. A particularly preferred polyurethane is one sold by Miles Inc. under the tradename DISPERCOLL U-42 which is provided in the form of an aqueous solution in which an aliphatic diisocyanate monomer and a polyol monomer are evenly dispersed. Upon evaporation of the aqueous solution the monomers polymerize.

The matrix material may be compounded with fillers such as carbon black, silica, glass microballoons, etc. up to an amount not to exceed about 300% by weight of the matrix material, preferably not to exceed 100% by weight. The polyurethane matrix material can also be blended with other water soluble polymeric compositions.

As explained in more detail below, an advantage of the thermoplastic polyurethane matrix material used in the invention is that it is water soluble.

A simple composite can be formed from the matrix-impregnated high strength fiber networks. "Simple composite" is intended to denote an article that includes at least one fiber network combined with a single major matrix material to form a unitary layer, whether or not there are other materials present such as fillers, lubricants or the like. Simple composite materials may be constructed and arranged in a variety of forms.

The matrix-impregnated fiber network also can be used to form more complex composites. For example, the composite can include a second matrix material in addition to the thermoplastic polyurethane. In a preferred embodiment the second matrix material is in the form of a film which is adjacent to at least one side of the matrix-impregnated fiber network. The matrix-impregnated fiber network can be pressed or embedded into the second matrix material so that the second matrix material at least partially encompasses the impregnated fibers.

Among second matrix material films which can be used in the invention are thermoplastic polyolefins, thermoplastic elastomers, crosslinked thermoplastics, crosslinked elastomers (e.g., ethylene propylene diene and butyl rubber), polyester, polyamide, fluorocarbon, urethane, epoxy, polyvinylidene chloride, and polyvinyl chloride. Homopolymers or copolymers of these films preferably are uniaxially or biaxially oriented.

It is especially preferred that the film be made of high density polyethylene (preferably having a melting point of about 105 °C), polypropylene, or a blend of polyethylene and styrene-isoprene-styrene block copolymer (available from Raven Industries). Such a film acts as an oxygen barrier, provides surface modification and allows for the separation of individual layers after they have been manufactured prior to molding of the final article.

In the preferred case of high density polyethylene film, a film thickness of about 4 to 80 μm , preferably 15 to 25 μm , is used and a pressure of about 0.001 to 1.5 kg/mm², and a temperature, preferably of about 60 to 400 °C, more preferably 100 to 160 °C, are employed for pressing the impregnated fiber network into the film.

It is convenient to characterize the geometries of such composites by the geometries of the fibers. One such suitable arrangement is a fiber network layer in which the fibers are aligned parallel to one another along a common fiber direction (referred to herein as a "unidirectionally aligned fiber network"). Successive layers of such unidirectionally aligned fibers can be rotated with respect to the previous layer. Preferably, the fiber network layers of the composite are cross-plyed, that is, with the fiber direction of the unidirectional fibers of each network layer rotated with respect to the fiber direction of the unidirectional fibers of the adjacent layers. An example is a five layer article with the second, third, fourth and fifth layers rotated +45°, -45°, 90° and 0° with respect to the first layer. A preferred example includes two layers with a 0°/90° layup. Such rotated unidirectional alignments are described, for example, in U.S. Patents No. 4,457,985; 4,748,064; 4,916,000; 4,403,012; 4,623,573; and 4,737,402.

In general, the composite of the invention is formed by the conventional method of applying the matrix material to the high strength fibers and then consolidating the matrix material/fibers combination. By "consolidating" is meant that the matrix material and the fiber network layer are combined into a single unitary layer. Consolidation can occur via drying, cooling, pressure or a combination thereof. Typically, however, consolidation is achieved substantially, if not completely, by drying.

For example, the fiber or yarn can be transported through a solution of the matrix material to substantially coat the fiber or yarn and then dried to form a coated fiber or yarn. The resulting coated fiber or yarn can then be arranged into the desired network configuration to form a layer of ballistic resistant material. Alternatively, the fiber network can be constructed initially and then coated with the resin matrix material or embedded into a film of the resin matrix material.

The fiber networks can be constructed via a variety of well known methods. In the preferred case of unidirectionally aligned fiber networks yarn bundles of high strength filaments, preferably having about 30 to about 2000 individual filaments of less than about 12 denier, and more preferably of about 100 individual filaments of less than about 7 denier, are supplied from a creel and led through guides and a spreader bar into a collimating bar prior to coating or impregnating with the matrix material. The collimating comb aligns the filaments coplanarly and in a substantially unidirectional fashion.

The fiber network layers typically contain from about 6 to 12 fiber ends per inch (2.4 to 4.7 ends per cm) and preferably 8 to 11 ends per inch (3.2 to 4.3 ends per cm). Each layer (including matrix material) is typically from about 0.01 to 0.2, preferably about 0.04 to 0.12, and most preferably about 0.06 to 0.10, mil (mm) thick.

In the instances of a simple composite where the matrix material is supplied in the form of a film, U.S. Patent No. 5,173,138, hereby incorporated by reference, describes a method for making the matrix material-impregnated fibrous network of the present invention. This method includes feeding a matrix film onto at least one side of the fiber network layer while heating for a time sufficient to impregnate the fiber network with the film without damaging the fibers and physical properties of the resin matrix.

Alternatively, the fiber network layer can be sandwiched between release papers, one of which is coated with the wet matrix material. This system is then passed under a series of pressure rolls to complete the impregnation of the fibers. The top release paper is pulled off while the impregnated network of fibers is subjected to heat to remove the solvent from the matrix material.

The preferred method, however, includes initially forming the fiber network layer, preferably a unidirectional network as described above, applying the matrix material onto the fiber network layer, and then drying the matrix material-impregnated fiber network layer as described, for example, in U.S. Patent No. 4,820,568, incorporated herein by reference. As shown in Figure 1, yarn is supplied from a creel 102 and passed through a combing station 104 to form the fiber network. The fiber network then is placed on a carrier web which can be a paper or a film substrate 106. The matrix material is applied to the fiber network layer by coating a solution of the matrix material onto the fiber network layer at 108. The coated fiber network then is passed through a pair of rollers 110. The rollers spread the matrix material substantially uniformly among the fibers. The impregnated fiber network layer is then passed through a heated oven 112 for drying. Nip roller 114 is used to control final layer thickness. Nip roller 116 is used to pull the carrier web and prepreg through the system. The substrate and the impregnated fiber network layer can then be wound on roller 118. In the oven, the impregnated fiber network layer is subjected to sufficient heat to volatilize the solvent for the matrix material.

Since previous matrix materials needed organic solvents having a high boiling point, the temperature and amount of oven residence time required were substantial. For example, a common conventional matrix material is a polyester or vinyl ester that requires a styrene solvent, which has a boiling point of 145°C. In order to volatilize the styrene, the impregnated fiber network must be pre-heated and transported through an oven approximately 30 m long at an oven temperature of 110-120°C. Since the matrix material of the present invention is water soluble and water has a lower boiling point than styrene, the required oven temperature is only about 88-99°C and the oven length is only about 10 m. The advantage of the shorter oven length is that the alignment of the fiber network does not tend to alter substantially as it passes through the oven. In ovens reaching up to about 30 m the dimensional stability of the individual fibers tends to diminish. Consequently, the fibers begin to have random curves and kinks that compromise the intended fiber alignment.

Another common matrix material is a styrene-isoprene-styrene block copolymer available from Shell Chemical under the trade name Kraton® D1107, which requires a methylene chloride solvent that necessitates extensive disposal measures. A further advantage of a water solvent is that it does not involve the handling and disposal problems associated with organic solvents such as methylene chloride.

If the second matrix material is desired, a preferred method for making the fiber network layer employs a separate film of a second matrix material upon which the high strength fiber or yarn is disposed and then coated. More specifically, the high strength fibers are transported through a comb means which collimates the fibers to form a unidirectionally aligned fiber network. The unidirectional fibers are laid onto a moving film of the second matrix material. A solution of the polyurethane matrix material then is coated onto the fibers which are laying on the film, thereby adhering the fibers to the film. The polyurethane matrix material may penetrate between the fibers and the film and should occupy substantially all the void space between the fibers, although some void spaces may remain. The polyurethane matrix material is subsequently dried. The coating and drying steps can be repeated to achieve the desired amounts of matrix material relative to the amount of fiber. An apparatus for carrying out this method is described in U.S. Patent No. 5,149,391, hereby incorporated by reference.

The proportion of matrix material to fiber in the composite may vary widely, depending upon the end use. If the density of the matrix material is similar to that of the fiber, then the matrix material may generally form from about 10 to about 40% by weight, preferably about 14 to 30%, more preferably 16 to 28%, and most preferably about 20 to 24%, based on the weight of an individual layer or the final composite. For ballistic resistant composite articles, the preferred range is up to 28% by weight. If the densities of the matrix material and fiber are dissimilar, then the matrix material may form from about 5 to about 40% by volume, preferably about 6 to 30%, more preferably 7 to 24%, and most preferably about 8 to 22%, based on the volume of an individual layer or the final composite. In the embodiments which include a second matrix material, then the polyurethane matrix material may generally form from about 5 to about 35% by weight, preferably about 10 to 28%, and most preferably about 20 to 24%, and the second matrix material may correspondingly generally form from about 5 to about 30% by weight, preferably about 6 to 14% by weight, more preferably 7 to 14%, and most preferably about 8 to 12%, based on the weight of the layer or the final composite.

The individual consolidated fiber network layers can be laid up into a stack for formation into the end use composite or they can be formed into a prepreg element which is subsequently used to form the end use composite. By "end use composite" is meant the integral multi-layer composite which is used in an article such as a helmet, military vehicle armor plates and sails. As mentioned previously, the most preferred composite is one wherein the fiber network of each layer is unidirectionally aligned and oriented so that the fiber directions in adjacent layers are in a 0°/90° configuration.

In the most preferred embodiment, two fiber network layers are cross-plyed in the 0°/90° configuration and then molded to form a prepreg element. The two fiber network layers can be continuously cross-plyed, preferably by cutting one of the networks into lengths that can be placed successively across the width of the other network in a 0°/90° orientation. U.S. Patent No. 5,173,138 describes an apparatus for continuous cross-plying. As described in PCT Publication No. WO 91/12136, the resulting continuous ply can then be wound into a roll with a layer of separation material between each ply. The roll is then subjected to pressure and/or heat in order to adhere the two cross-plyed fiber networks together.

The temperatures and/or pressures to which the fiber network layers are exposed for molding vary depending upon the type of high strength fiber used. The end use composite for use in armor panels can be made by molding a stack of fiber network layers or prepreg elements under a pressure of about 150 to 400, preferably about 180 to 250, psi and a temperature of about 220 to 260 °F. The end use composite for use in helmets can be made by molding a stack of fiber network layers or prepreg elements under a pressure of about 1500 to 3000, preferably about 1800 to 2200, psi and a temperature of about 220 to 260 °F.

If the composite is intended for use as a sailcloth material, one 0°/90° element is typically employed. An important advantage of this element is that it is capable of adhering to other materials frequently used in sailcloth construction. For example, the most preferred construction is one 0°/90° element adhered to a Mylar® polyester film available from DuPont.

The following examples are presented to demonstrate the advantages of the invention. The specific techniques, conditions, materials, proportions and reported data set forth to illustrate the principles of the invention are exemplary and should not be construed as limiting the scope of the invention.

The total areal density (ADT) indicates the weight of fiber and matrix material per unit area of an individual fiber network layer.

Fragment ballistic testing of the examples was performed in accordance with Military Specification MIL-P-662E using a fragment simulation projectile (FSP) in accordance with the specifications of Military Specification MIL-P-46593A. Bullet ballistic testing of the examples was performed in accordance with National Institute of Justice (NIJ) standard 0101.03. According to this method, samples are prepared, placed on a clay backing, and shot 16 times with a 7.62 mm. The protective power of the sample is expressed by citing the impacting velocity at which 50% of the projectiles are stopped which is designated the V₅₀ value.

Each example includes at least one panel molded from a stack of 37 prepreg elements that each have two unidirectional fiber network layers arranged in a 0°/90° configuration. The fiber is 1300 denier extended chain polyethylene yarn available from AlliedSignal under the tradename Spectra® 1000 and it is embedded in a thermoplastic polyurethane matrix material that is available from Miles Inc. under the tradename DISPERCOLL U-42. The DISPERCOLL U-42 has a reported tenacity of 1600 psi, a tensile modulus (100% elongation) of 220 psi, a tensile modulus (300% elongation) of 410 psi, and an elongation-to-break of 850%. Each fiber network layer has 22% by weight of matrix material and 78% by weight fiber and 8 to 10 yarn ends per inch. Each panel is 12 inches by 12 inches. The areal density and number of panels varies for each example. The stack of prepreg elements is molded at a temperature of 24-250 °F and a pressure of 200 psi for a period of 20 minutes in order to make the panel. Table 1 shows the ballistic

performances of the examples. "Shot/panel" indicates the number of shots required before the panel was destroyed.

The comparative examples are composites having the same structure of the inventive examples except that a styrene-isoprene-styrene block copolymer available from Shell Chemical under the trade name Kraton® D1107 is substituted as the matrix material.

Table 1

Example	AD/Panel (lb/Ft ²)	Threat	# Panels	Shot/Panel		V ₅₀ (ft/sec)	
				Inv.	Comp.	Inv.	Comp.
1	1.96,1.95	.30FSP	2	6	4-6	2101	2000
2	2.98,2.90	.30FSP	2	5-6	4-6	2822	2600
3	1.89,1.88,1.91, 2.03,2.08,2.06	.50FSP	6	1	1	1514	1600
4	3.94,3.80,3.89	7.62mm	3	2-3	2-3	2837	2750
5	4.85,4.89,4.88	7.62mm	3	2	2-3	3273	3100

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

Claims

1. An article comprising at least one network of high strength fibers in a matrix material, the high strength fibers having a tenacity of at least about 7 g/d, a tensile modulus of at least about 150 g/d and an energy-to-break of at least about 8 J/g, wherein the matrix material comprises a thermoplastic polyurethane derived from an aliphatic diisocyanate and a polyol.
2. An article according to claim 1, wherein the high strength fibers comprise extended chain polyethylene fibers.
3. An article according to claim 1, wherein the aliphatic diisocyanate is selected from at least one of the group consisting of hexamethylene diisocyanate, trimethyl hexamethylene diisocyanate, hydrogenated 4,4'-methylene diisocyanate, m-trimethyl xylene diisocyanate and isophorone diisocyanate.
4. An article according to claim 1, wherein the polyol comprises a polyester polyol.
5. An article according to claim 1, wherein the aliphatic diisocyanate comprises a combination of a hexamethylene diisocyanate and an isophorone diisocyanate and the polyol comprises a polyester polyol.
6. An article according to claim 1, wherein the polyurethane matrix material has a tenacity of about 1300 to 1900 psi (8970 to 13110 kPa), a tensile modulus (at 100% elongation) of about 190 to 250 psi (1311 to 1725 kPa), a tensile modulus (at 300% elongation) of about 375 to 450 psi (2587 to 3105 kPa), a T_g of less than about 80 °C, and an elongation-to-break of at least about 650 to 1000%.
7. An article according to claim 1, wherein the article is a ballistic resistant composite.
8. A prepreg element comprising at least two adjacent layers of a network of high strength fibers in a matrix material, the high strength fibers having a tenacity of at least about 7 g/d, a tensile modulus of at least about 150 g/d and an energy-to-break of at least about 8 J/g, wherein the matrix material comprises a thermoplastic polyurethane derived from an aliphatic diisocyanate and a polyol.
9. A prepreg element according to claim 15, wherein the high strength fibers comprise extended chain polyethylene fibers.

10. A prepreg element according to claim 10, wherein the aliphatic diisocyanate comprises a combination of a hexamethylene diisocyanate and a isophorone diisocyanate and the polyol comprises a polyester polyol.

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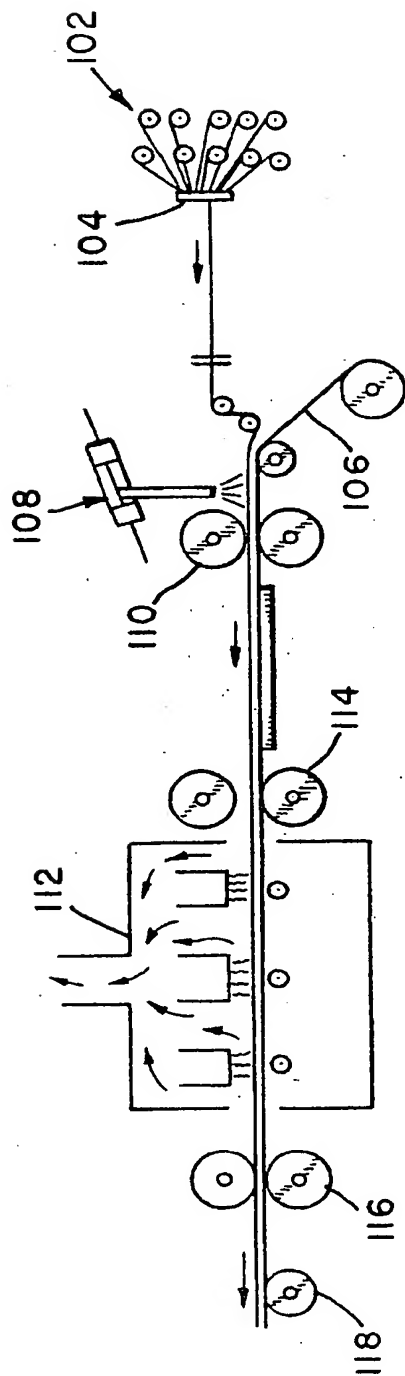


FIG. 1



European Patent
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PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention EP 94 11 3278
shall be considered, for the purposes of subsequent
proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO-A-92 00191 (COCHRAN W.H.) * claims * * examples 1,2 * * page 14, line 1 - line 5 * ---	1-4,7	C08J5/04 //C08L75:04
X	KUNSTSTOFFE, vol.82, no.12, 1992, MUNCHEN, DE pages 1181 - 1184, XPO00330339 STEINBERGER R. ET AL 'Glasfaserverstärkte thermoplastische Polyurethane' * the whole document * ---	1,3,4	
X	EP-A-0 111 122 (BASF AKTIENGESELLSCHAFT) * claims 1,6,9,10 * * page 7, line 23 - line 32 * ---	1,3-5	
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 93-024299[03] & JP-A-4 353 525 (TOYOCO KK) 8 December 1992 * abstract * ----- -/--	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08J C08L
INCOMPLETE SEARCH			
<p>The Search Division considers that the present European patent application does not comply with the provisions of the European Patent Convention to such an extent that it is not possible to carry out a meaningful search into the state of the art on the basis of some of the claims</p> <p>Claims searched completely:</p> <p>Claims searched incompletely:</p> <p>Claims not searched:</p> <p>Reason for the limitation of the search:</p> <p>see sheet C</p>			
Place of search		Date of completion of the search	Examiner
THE HAGUE		9 January 1995	Niaounakis, M
CATEGORY OF CITED DOCUMENTS			
<p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p>		<p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>-----</p> <p>& : member of the same patent family, corresponding document</p>	



EP 94 11 3278

-C-

INCOMPLETE SEARCH

Claims searched completely: 1-8

Claims not searched: 9,10

Claims not searched refer to either non-existing claims or to themselves and therefore, they do not comply with the requirements of article 84 when read in conjunction with Rule 29(4) of the European Patent Convention.